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⑨ Wettable, flexible, oxygen permeable contact lens containing block copolymer
polysiloxane-polyoxyalkylene backbone units.

⑩ Contact lenses which are optically clear, wettable, flexible, and of high oxygen permeability in the aqueous
ocular environment of use, of a block copolymer containing polysiloxane and polyoxyalkylene oxide units are
disclosed, as well as the preparation thereof and methods of treating vision defects therewith.

Wettable, Flexible, Oxygen Permeable Contact Lens Containing Block Copolymer Polysiloxane-Polyoxyalkylene Backbone Units

This invention relates to ophthalmic devices, such as contact lenses and intraocular implants, and particularly contact lenses of a block copolymer containing polysiloxane and polyoxyalkylene oxide units possessing an advantageous blend of desirable properties including a) high oxygen permeability, b) good wettability, c) flexibility and d) optical clarity, in the ocular environment of use. The invention further relates 5 to the polymers from which the ophthalmic devices are fabricated and the special macromers used to prepare the polymers.

The use of siloxane containing materials of various types in the fabrication of ophthalmic devices is well known.

Thus, in U.S. 3,996,187; 3,996,189; 3,341,490 and 3,228,741 there are described contact lenses 10 fabricated from poly(organosiloxanes) containing fillers. While such lenses are generally soft and of high oxygen permeability, the use of fillers such as silica, is indicated in order to increase the otherwise generally poor tear strength and tensile strength. Also, such silicone rubber lenses are characteristically both hydrophobic and lipophilic.

U.S. 3,808,178 discloses hard contact lenses fabricated from copolymers of a polysiloxanylalkyl acrylate 15 or methacrylate ester and an alkyl acrylate or methacrylate ester. The monomers and polymers of the patent are hydrophobic and are incompatible with hydrophilic materials such as hydroxyethyl methacrylate. While the disclosed lenses have increased oxygen permeability, they are rigid.

U.S. 4,136,250 discloses hydrogels of a copolymer of about 20 to about 90 % of a hydrophilic (or mixture of hydrophilic and hydrophobic) monomer and about 10 to about 80 % of a polyolefinic siloxane 20 macromer which can be used to fabricate a contact lens. Typically, such materials are recited to possess a degree of swelling of about 10 to about 12 %. It has been found, however, that the presence of substantial amounts of water therein limits the oxygen permeability of such materials.

U.S. 4,153,841 relates, in relevant part, to contact lenses fabricated from a polymer of a polyorganosiloxane terminated with vinylic groups, or copolymers thereof with other monomers. The exemplified 25 products therein are hydrophobic in nature.

U.S. 4,486,577 relates to copolymers of about 8 to 70 % of a polysiloxane macromer containing at least two vinyl groups and 30-92 % of a monomer which is at least predominantly water insoluble to make polymers useful, for example, as contact lenses.

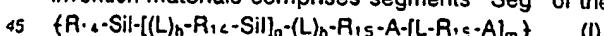
Generally, such prior art contact lens compositions are either insufficiently hydrophilic in terms of 30 surface wettability to be acceptable to the contact lens profession, even though they may possess high oxygen permeability, or such contact lenses are of acceptable wettability but the hydrophilicity is coupled with water swellability, which tends to limit optimum oxygen permeability.

It is an object of the present invention to overcome these and other disadvantages of the art by 35 providing ophthalmic devices, such as contact lenses and corneal implants, possessing a high degree of surface wettability and possessing a high degree of oxygen permeability notwithstanding their swellability by employing a crosslinked block polymer containing polysiloxane and polyoxyalkylene oxide units.

A further object of the invention is to provide a method of correcting visual defects in the form of refractive errors by fitting to the patient's eye in need of the same a corrective contact lens of such 40 polymer. These and other objects of the invention are apparent from the following detailed description of the invention.

Another object of the invention is to provide novel macromers for accomplishing the above objects.

The present invention is directed to macromers, polymers derived therefrom, ophthalmic devices obtained from such polymers as well as methods of manufacturing each of the foregoing. Each of the above 45 invention materials comprises segments "Seg" of the formula

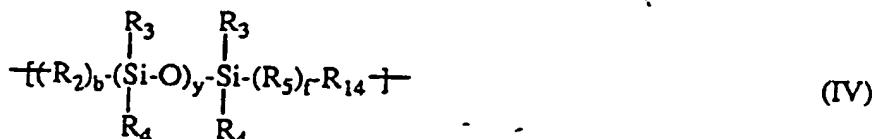


wherein Sil is a divalent poly(disubstituted siloxane), A is a divalent polyoxyalkylene oxide (which may be substituted), R₁₄ is oxygen or an amino nitrogen, R₁₅ is a bond, an amino nitrogen, or, when the adjacent atom of Sil is other than silicon, it may also be oxygen, L is a divalent linking group, n is an integer of 0 to 3, and m is an integer of 0 to 10.

The present invention relates to novel macromers, polymers fabricated therefrom, ophthalmic devices prepared from the polymers (especially contact lenses and intraocular lenses), as well as methods of manufacture of each. The ophthalmic devices ultimately fabricated are optically clear, hydrolytically stable, biologically inert, wettable, flexible, of good mechanical strength, oxygen permeable, and when fully swollen in their environment of use have a water content of at least 10 %.

- The macromer is a reactive monomer having a segment "Seg" of the formula
 $\{R_{14}\text{-Sil-}[(L)_h\text{-}R_{14}\text{-Sil}]_n\text{-}(L)_k\text{-}R_{15}\text{-A-[L-R}_{15}\text{-A]}_m\}$ (I)
more preferably a segment "Grp" of the formula
 $\{R_{15}\text{-A-[L-R}_{15}\text{-A]}_m\}_{\overline{a}}\text{-}(L)_k\}_{\overline{a}}\text{-}(Seg\text{-}(L)_h\text{-}R_{14}\text{-Sil-}[(L)_h\text{-}R_{14}\text{-Sil}]_n\}_{\overline{a}}$ (II)
5 and most preferably the monomer is of the formula
Cap-Grp-Cap (III)
wherein "Cap", "Grp" and "Sil" are singular variables (i.e. the "a" within "Cap" is not a separate variable);
a is zero or 1;
e is zero or 1;
10 a plus e is 1;
h is 1, but may also be zero when the atom of Sil, to which it would otherwise be attached, is a carbon atom;
n is zero to 3;
m is zero to 10, preferably zero to 3;
15 p is zero to 7;
each R_{14} is a bond, $-N(R\cdot)$, or $-O-$ except that R_{14} cannot be $-O-$ if it is attached directly to a silicon atom;
 R_{15} is $-O-$ or $-N(R\cdot)$, with $R\cdot$ being hydrogen, C_{1-12} -alkyl, or phenyl;
each Sil is independently of the formula

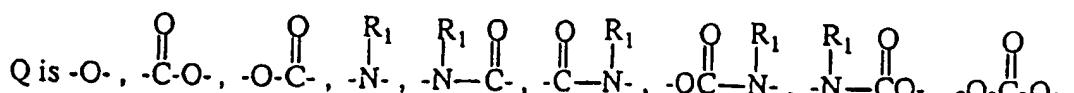
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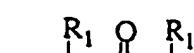
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- in which R_2 and R_5 are each independently branched C_{1-12} -alkylene, carbonyl, C_{1-6} -alkylene carbonyl, C_{1-6} -alkylene-(oxy-C₁₋₆-alkylene)_g- [g being an integer of 1 to 10], or C_{1-6} -alkylene-O-CH₂-(hydroxy C₁₋₆-alkylene)-CH₂-;
- 30 each b and f is independently 0 or 1;
-
- each
- R_3
- and
- R_4
- is independently selected from
- C_{1-18}
- alkyl and aryl of up to 12 carbon atoms; and
-
- each y is independently 1-200;
-
- each L is independently selected from -L
- ₁
- R
- ₆
- L
- ₂
- wherein L
- ₁
- and L
- ₂
- are each independently
-
- 35
- $\begin{array}{c} O \\ || \\ -C-O- \end{array}$
- or
-
- $\begin{array}{c} O \\ || \\ -C-NH- \end{array}$
- in which the oxygen or amino nitrogen respectively is bound to R
- ₆
- , or independently L
- ₁
- and L
- ₂
-
- may also independently be
-
- 40
- $\begin{array}{c} O \\ || \\ -C- \end{array}$
- or a bond, and each R
- ₆
- is independently selected from
-
- i) a divalent aliphatic group of up to 25 carbon atoms;
-
- ii) a group of the formula
-
- $-(C_{1-20}\text{aliphatic})_jQ_k\text{-}\{(5-7 membered cycloaliphatic or aryl of up to 25 carbon atoms)}-Q_{(k1)}\text{-}(C_{1-20}\text{aliphatic})_{j1}\text{-}D-$
- (IX),
-
- 45 each of j, k, k
- ₁
- and j
- ₁
- being independently zero or one, but if j is 0, then k is 0 and if j
- ₁
- is 0, then k
- ₁
- is 0;
-
- wherein each aliphatic group in i) and ii) above may be interrupted at any point by Q, and each aliphatic, cycloaliphatic and aryl group in i) or ii) may be singly or multiply substituted by one or more of halogen, hydroxy,
- C_{1-12}
- alkyl, carboxy or
- C_{1-12}
- perhaloalkyl;

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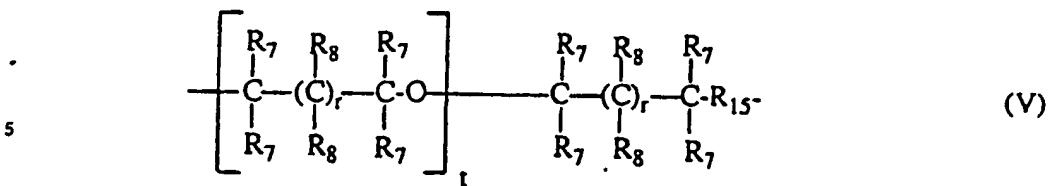


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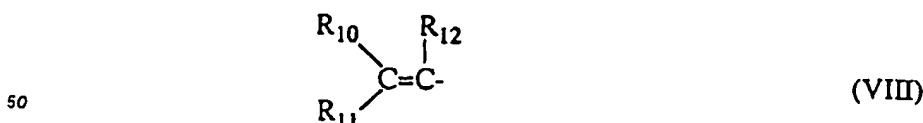
or $-N-C-N-$; and D is 1 to 3;

each A is independently of the formula



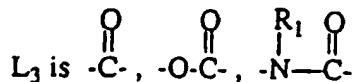
wherein each r is 0-4:

- 10 t is 3-200, in which preferably at least 30 %, more preferably at least 50 %, still more preferably at least 75 %, most preferably 100 %, of the A groups of formula V within any one macromer of formulae I-III are limited to having homopolymeric sub-blocks of not more than 15 repeating units, preferably not more than 10 repeating units, more preferably not more than 7 repeating units, most preferably not more than 4 repeating units: each R₇ is independently selected from groups i) and iii) below and each R₈ is independently selected from groups ii)-iv) below:
- 15 i) hydrogen, halogen, unsubstituted C₁₋₆alkyl, substituted C₁₋₆alkyl, unsubstituted C₂₋₆alkenyl, and substituted C₂₋₆alkenyl, wherein a) the substituents on the alkyl and alkenyl groups in i) are independently selected from fluoro, C₁₋₆alkoxy, C₂₋₆alkanoyloxy, C₁₋₆alkoxy-C(O)-, C₂₋₆alkenyoxy-C(O)-, C₃₋₈alkenyoxy, aryl of up to 10 carbon atoms, aryloxy of up to 10 carbon atoms, aroyl of up to 11 carbon atoms, aroyloxy of up to 11 carbon atoms, aryl (of up to 10 carbon atoms)-oxycarbonyl, C₃₋₈cycloalkyl, C₃₋₈cycloalkoxy, (C₃₋₈cycloalkyl)-carbonyloxy, (C₃₋₈cycloalkoxy)carbonyl, oxacycloalkyl of up to 7 carbon atoms, oxacycloalkoxy of up to 7 carbon atoms, oxacycloalkoxy (of up to 7 carbon atoms)-carbonyl, and oxacycloalkyl (of up to 7 carbon atoms)-carbonyloxy; and b) each alkyl and alkenyl group in a) being unsubstituted or further substituted by fluoro, C₁₋₆alkyl, or C₁₋₆alkoxy provided that said last mentioned alkoxy is not bound to a carbon already singly bound to another oxygen atom; and
- 20 ii) C₁₋₆alkoxy, C₂₋₆alkanoyloxy, C₁₋₆alkoxy-C(O)-, C₂₋₆alkenyoxy-C(O)- and C₃₋₈alkenyoxy, each of which may be further substituted by fluoro, aryl of up to 10 carbon atoms, or C₁₋₆alkoxy provided that the last mentioned alkoxy is not bound to a carbon atom which is singly bound to another oxygen;
- 25 iii) aryl of up to 10 carbon atoms, C₃₋₈cycloalkyl, and oxacycloalkyl of up to 7 carbon atoms, each of which is unsubstituted or substituted by a substituent selected from those indicated in i)a) and b) above;
- 30 iv) aryloxy of up to 10 carbon atoms, cycloalkoxy of up to 8 carbons, cycloalkyl (of up to 8 carbons)-C(O)O-, cycloalkoxy (of up to 8 carbons)-carbonyl, aroyloxy of up to 11 carbons, oxacycloalkoxy of up to 7 carbons, oxacycloalkenyoxy of up to 7 carbons, oxacycloalkoxy (of up to 7 carbon atoms)-carbonyl, oxacycloalkyl (of up to 7 carbon atoms)-carbonyloxy, aryloxy of up to 11 carbon atoms, and aroyloxy of up to 11 carbon atoms, each of which is unsubstituted or substituted by fluoro, C₁₋₆alkyl, or C₁₋₆alkoxy, provided said last mentioned alkoxy is not bound to a carbon atom which is singly bound to another oxygen; and 2 adjacent groups R₇ and R₈, together with the atoms to which they are attached may define a 5-8 membered cycloalkyl, cycloalkenyl, or oxacycloalkyl ring or a 6-14 membered bicyclo-ring.
- 35 Each Cap is independently selected from
- 40 i) a vinyl containing group of the formula R₁₋₆(L₄)_z(R₆)_w(A₁₋₆)_x(J(R₉)_M(L₅)_G(R₆)_H(L₆)_I)_Z (VI)
- or ii) a group of the formula R₁₋₇(L₄)_z(R₆)_w(A₁₋₆)_x(J(R₉)_M(L₅)_G(R₆)_H(L₆)_I)_Z (VII)
- 45 at least one Cap per macromer being of formula VI; wherein R₁₋₆ is of the formula

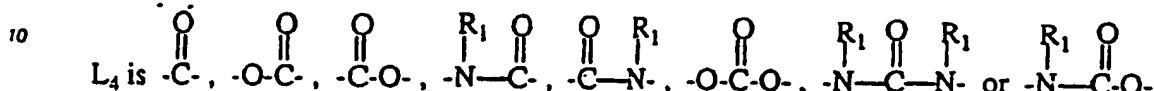


in which R₁₋₂ is hydrogen or C₁₋₆alkyl and each of R₁₀ and R₁₁ is independently hydrogen, C₁₋₆alkyl, or -COOR₁₃ with R₁₃ being hydrogen or C₁₋₆alkyl;

55 w, x and z are each independently zero or one but if w is zero, one of x and z must be zero;



5 with the right hand portion attached to Grp provided that the Grp atom to which L_3 is attached is not a carbonyl carbon, an amido nitrogen or a carboxy oxygen and L_3 is -O- or -NR₁- when such Grp atom is a carbonyl carbon;



15 when w is one, and selected from the same group as L_3 when w is zero;



25 L_5 is -C(O)NH- with the carbonyl attached to R₉ or J;
 L_6 is -C(O)NH- with the nitrogen attached to R₆ or R₉;
J is -O- or -NH-;
G, Y, M, T, V, and Z are independently 0 or 1, but if Y is zero, then G is zero and M is one; and



35 and R₁₇ is selected from
a) H, NH₂, OH, -NCO, -NCS, -C(O)-halogen and COOR₁₂ when the non-R₁₇ atom to which it is attached is a non-carbonyl saturated carbon or the non-R₁₇ atom to which it is attached is a carbon which is part of a ring;
b) H, -C(O)-halogen, -C(O)-R₁₂, -C(O)-OR₁₂ and R₁₂ when the non-R₁₇ atom to which it is attached is an oxygen other than a carboxy oxygen;
c) H and R₁₂, when the non-R₁₇ atom to which it is attached is a carboxy oxygen;
d) -C(O)-R₁₂, -C(O)-OR₁₂, -C(O)N(R₁)R₁₂ and R₁₂ when the non-R₁₇ atom to which it is attached is an amino nitrogen, or R₁₂ when the non-R₁₇ atom to which it is attached is an amido nitrogen;
e) OH, R₁₂, CH₂C(O)R₁₂, CH₂C(O)OR₁₂, NH₂, and -NHR₁₂ when the non-R₁₇ atom to which it is attached is a carboxy carbon; and
f) H, OH, halogen, -OR₁₂ when the non-R₁₇ atom to which it is attached is silicon.

Similar macromers and e.g. polymers thereof are disclosed in European Patent Applications 330,616, 330,617 and 330,618. However, the residues R₂ and R₅ of Sil (formula IV) of the present invention are different from the corresponding residues in the above mentioned applications.

50 The macromers of formulae I, II and III or mixtures thereof are polymerized into polymers which may be shaped into ophthalmic devices such as intraocular implants and contact lenses or utilized as active agent releasing materials, especially release rate controlling membranes or matrices in transdermal drug delivery devices or as tablet release matrices in various applications. The polymers and ophthalmic devices of the invention will swell, when in contact with sufficient aqueous medium, until a fully swollen water content of from at least 10 % to about 95 % has been reached.

55 The ophthalmic devices and polymers of the invention exhibit a receding contact angle of less than 60; the measurement of which is conveniently performed using a modified "Wilhelmy Plate" technique, as described for example in J.D. Andrade et al, Surface and Interfacial Aspects of Biomedical Polymers, Vol. 1,

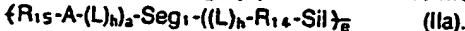
Surface Chemistry and Physics, Plenum Press, 1985, wherein a specimen sample, in the form of a plate of known dimensions, is immersed into the wetting solution, pure water, at a slow controlled rate, e.g. at 2-20 mm per minute.

The invention ophthalmic devices also have a high oxygen permeability, Dk. Dk is measured using a modification of ASTM standard D3985-81 in that a) 21 % oxygen, i.e. air, is used instead of 99-100 % oxygen, b) 0.5 m² surface area is used instead of 100 m², and c) the humidity is 95-100 % relative humidity instead of 0 % relative humidity. Typically, conventional, fully swollen polyhydroxyethylmethacrylate (pHEMA) lenses which are sparingly crosslinked have a Dk of 5-7 ($5.7 \times 10^{-10} \text{ mm}^2 \text{ sec}^{-1} \text{ mmHg}^{-1}$) or $5.7 \times 10^{-10} \text{ cm/sec}$. The ophthalmic devices of the instant invention have oxygen permeability Dk values generally greater than 7-10 (10^{-10} cm/sec).

Preferred macromers of formulae I, II and III are those wherein n is zero or one, most preferably zero. Another group of preferred macromers of formulae I-III are those where m is 0-4, more preferably zero or one, most preferably zero. A highly preferred group of macromers of formulae I-III are those wherein both m and n are zero or one, most preferably both m and n are zero, to result in Seg₁, a most highly preferred embodiment of Seg₁ of the formula



and Grp₁, a most highly preferred embodiment of Grp₁ of the formula



Within Sil above, b and f are each independently preferably one, with a highly preferred embodiment being when both b and f are one;

R₂ and R₅ are each independently preferably branched C₃-alkylene, C₁₋₄alkylene-(oxy-C₂₋₄alkylene)_g (wherein g is 1-10, preferably 1-4, more preferably 1-2, most preferably 1) or C₂₋₄alkylene-oxy-CH₂-(hydroxy-C₁₋₂alkylene)-CH₂, more preferably C₁₋₄alkylene or -CH₂-(OC₂H₄)_g with g preferably 1 or 2, most preferably 2.

Within Sil of formula IV, y is preferably 5 to 100, more preferably 10 to 50, most preferably 20 to 30. A particularly useful subembodiment has y = 25 to 29, especially when a is 1 and e is zero.

R₁₄ is preferably a bond or -O-, more preferably -O-.

R₁ is preferably methyl or hydrogen, more preferably hydrogen.

Each R₃ and R₄ is independently preferably C₁₋₃alkyl or phenyl, more preferably C₁₋₃alkyl, still more preferably methyl or ethyl, most preferably methyl. A most preferably embodiment of Sil is when all of R₃ and R₄ are the same.

R₁₅ is preferably -O- or -NH-, more preferably -O-.

Each h is independently preferably 1, most preferably each h is one.

p is preferably 0 to 5, still more preferably 0 to 3, most preferably 0 or 1.

As stated above, the linking group L is L₁R₆L₂ wherein L₁ and L₂ are independently -COO- or -C(O)NH- (in which the oxygen or amido nitrogen is bound to R₆) or -C(O)- or a bond. Preferably, each L₁ and L₂ is independently -COO-, -C(O)NH-, or -C(O)-, more preferably -COO-, or -C(O)NH- and most preferably -C(O)NH-.

In a most highly preferred embodiment, all of the L₁ groups are the same and all of the L₂ groups are the same. In a still more highly preferred subembodiment, L₁ and L₂ are the same groups.

Each R₆ is preferably independently selected from

i) a divalent aliphatic group of up to 12 carbon atoms, preferably up to 7 carbon atoms, more preferably up to 4 carbon atoms;

ii) -(C₁₋₂aliphatic)-Q_k-(5-7 membered cycloaliphatic or aryl of up to 25 carbon atoms)-Q_{k1}-

(C₁₋₂aliphatic)_{j1}o- each of j, k, k₁ and j₁ being 0 or 1 but if j is zero, k must be zero and if j₁ is zero, k₁ must be zero; preferably each of the C₁₋₂aliphatic groups in ii) are C₁₋₁₂aliphatic, more preferably C₁₋₇aliphatic, still more preferably C₁₋₄aliphatic, most preferably C₁₋₂aliphatic; preferably the C₅-cycloaliphatic is C₆cycloaliphatic, most preferably a cyclohexane; preferably the aryl of up to 25 carbons is up to 14 carbons, more preferably up to 10 carbons, still more preferably of 6 carbons, most preferably a phenyl ring; preferably k is zero and preferably k₁ is zero, but most preferably k and k₁ are each zero; wherein each aliphatic group within i) and ii) above may be interrupted at any point by Q and each aliphatic, cycloaliphatic, and aryl group in i) or ii) is unsubstituted or substituted by one or more of halogen (preferably fluorine or chlorine, most preferably fluorine), hydroxy, C₁₋₄alkyl (preferably methyl, ethyl, propyl, or isopropyl, more preferably methyl or ethyl, most preferably methyl), carboxy, or C₁₋₁₂perhaloalkyl (preferably C₁₋₇perhaloalkyl, more preferably C₁₋₄perhaloalkyl, still more preferably perhalomethyl, perhaloethyl, or perhalopropyl, most preferably perhalomethyl, with the halogen atom being preferably the same and preferably fluorine or chlorine, most preferably fluorine. D is preferably 1 or 2, more preferably 1.

Most preferably, the R_6 aliphatic groups are not interrupted by Q, and preferably are unsubstituted. Also most preferably, the R_6 cycloaliphatic groups are substituted by 1-4 substituents, preferably 1-3 substituents, which substituents are preferably selected from halogen (preferably fluorine), hydroxy, and C₁-alkyl (preferably methyl, ethyl, propyl or isopropyl, most preferably methyl). In a most highly preferred embodiment each of the substituents is the same. Preferably, one of j and j1 is zero when the R_6 group

5 contains a cycloaliphatic. The most highly preferred cycloaliphatic containing R_6 is (5-yl-1,3,3-trimethylcyclohexyl)-methyl (the residue of isophorone diisocyanate absent the two isocyanate groups).

Preferably, the R_6 aryl groups are unsubstituted or substituted by 1-4 substituents, preferably unsubstituted or substituted by 1 or 2 substituents, more preferably unsubstituted or substituted by 1 substituent 10 which substituents are preferably selected from halogen (preferably fluorine), hydroxy, and C₁-alkyl, more preferably C₁-alkyl (preferably methyl, ethyl, propyl, or isopropyl, more preferably methyl). When more than one substituent is present per aryl, the substituents on any one aryl is preferably the same. A most highly preferred aryl embodiment of R_6 is toluenediyl.

A preferred subclass of R_6 includes: ethane-1,2-diyl; propane-1,2-diyl; propane-1,3-diyl; tetramethylene-diyl; hexane-1,6-diyl; cyclohexane-1,2-diyl; cyclohexane-1,3-diyl; 1,4-phenylene; bis[4-yl-cyclohexyl]-methane; bis(4-yl-cyclohexenyl)methane; bis(4-yl-phenyl)methane; toluene-2,4-diyl; toluene-2,6-diyl; m- and p-tetramethylene-diyl; toluene-1,2-diyl; toluene-1,4-diyl; 3,3'-dichloro-4,4'-diyl-biphenyl; naphthalene-1,5-diyl; dihydro-toluene-diyl; tetrahydrotoluene-diyl; (5-yl-1,3,3-trimethylcyclohexyl)methyl; trimethylhexane-1,6-diyl (especially 2,2,4-trimethylhexane-1,6-diyl and 2,4,4-trimethylhexane-1,6-diyl); diethylfumarate-2,2'-diyl; 1-20 carboxypentane-1,5-diyl; naphthalene-1,2-, 1,3-, 1,6-, 1,7-, 1,8-, 2,7, and 2,3-diyl; 1-methylnaphthalene-2,4- and -2,7-diyl; methylcyclohexane-1,4-diyl; 6,(7)-methylnaphthalene-1,3-diyl; biphenyl-4,4'-diyl; -3,3'-dimethoxybisphenyl-4,4'-diyl; 2,2'-dimethylbiphenyl-4,4'- and 3,3'-diyl; bis (4-ylphenyl)ethane; and bis(4-ylphenyl)ether.

The polyalkylene oxide groups are of formula V and are homo or copolymeric blocks having a total of 25 3-200 alkylene oxide units and an additional terminating alkylene oxide or amine. However, no homopolymeric subblock is in excess of 100 repeating units. Preferably, no individual A has a subblock in excess of 15 repeating units. The portion of the alkylene oxide alkylene chain in the macromer backbone is a straight chain of 2 (r is zero) to 6 (r is 4) carbon atoms which may be unsubstituted or substituted as set forth previously.

30 Preferably the number of alkylene oxide units (i.e. t) is 3-150, more preferably 4-100, still more preferably 5-75, still even more preferably 6-70. Within this group are two highly preferred subembodiments, a) those with t of 25-70, preferably 50-68, most preferably 60-66 and b) those with t of 8-50, preferably at least 9, more preferably at least 10, still more preferably 13-35, even more preferably 15-30, most preferably 20-25, especially about 22.

35 Also highly preferable are two embodiments wherein at least 30 % of the A groups within the macromers of formulas I-III consist of 32 % and 35 %, respectively, of polyethylene glycol and 68 % and 65 %, respectively of polypropylene glycol, the polyethylene glycol blocks being of no more than 3 repeating units each and the polypropylene glycol blocks being of no more than 7 repeating units each.

While it is highly preferable that each A be of the same structure throughout the macromer, there is no 40 such absolute requirement. Preferably at least 20 %, more preferably 25 %, still more preferably 33 %, yet more preferably 50 %, even more preferably 75 % and most preferably at least 90 % of the A groups within any one macromer are the same.

Within each A group, there are two highly preferred subembodiments:

- 45 a) homopolymeric A units,
- b) copolymeric A units of the 'EXE' type with the 'X' portion having approximately twice the number of repeating units as either 'E' (i.e. a poloxamer or reverse poloxamer like grouping).

While these two arrangements are highly preferred, other arrangements of alkylene oxide copolymeric type are also suitable.

50 Substituents on the alkylene oxide backbone portion (i.e. R_7 and R_8) are preferably selected from those set forth above. Preferably, each alkyl group within R_7 or R_8 whether alone or as a part of a larger group, has up to 4 carbon atoms, more preferably meth, ethyl, butyl, or t-butyl (provided that adjacent groups on a ring cannot each be t-butyl), most preferably methyl. Preferably, each alkenyl within R_7 or R_8 , whether alone or as part of a larger group has 2-4 carbons, and is more preferably C₂-alkenyl. An R_7 or R_8 aryl is preferably phenyl or naphthyl, most preferably phenyl. Cycloalkyl groups within R_7 and R_8 preferably have 55 5-6 ring members, most preferably 6 ring members. Oxacycloalkyl groups within R_7 or R_8 are preferably of 5-6 ring members, more preferably 6 members, each having only a single heteroatom in the ring which heteroatom is oxygen.

While the entire A unit may have a substantial fluorine substituent content, it is preferably at least 25 %

halogen free, more preferably at least 30 % halogen free, still more preferably at least 40 % halogen free, yet more preferably at least 60 % halogen free, and most preferably substantially halogen free.

- Preferably R_7 is hydrogen, $C_1\text{-alkyl}$ more preferably $C_1\text{-alkyl}$, more preferably methyl; substituted $C_1\text{-alkyl}$, most preferably substituted methyl; phenyl, substituted phenyl, benzyl, substituted benzyl, cyclohexyl, or $C_6\text{-oxacycloalkyl}$, preferably $C_6\text{-oxacycloalkyl}$; each of the "substituents" preferably being $C_1\text{-alkoxy}$ (more preferably $C_1\text{-alkoxy}$), fluorine, or when substituted on a group other than alkyl, $C_1\text{-alkyl}$; the most preferable substituents being methoxy, fluorine, and when substituted on other than alkyl, methyl. Substituents on aryls within R_7 are preferably in the *p*-position. R_8 is preferably selected from the same group as R_7 and $C_1\text{-alkoxy}$, phenoxy, and $C_6\text{cycloalkoxy}$, more preferably the same group as R_7 .

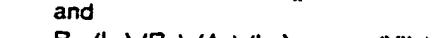
At least one Cap per macromer is independently of formulae VI or VII, but preferably the macromers have both Cap groups of formula VI. Most preferably, within each macromer the Cap groups are the same.

- Preferably, the Cap groups are of formula VI in which R_{16} is preferably a vinyl group of formula VIII in which R_{18} is hydrogen, R_{19} is hydrogen, $C_1\text{-alkyl}$ (preferably methyl), or -COOR_{13} , with R_{13} being hydrogen or methyl. More preferably the formula VI Cap groups have an R_{16} which is a vinyl of formula VIII in which R_{13} and R_{18} are each hydrogen and R_{12} is hydrogen or methyl.

Preferred Cap groups, whether of formula VI or VII are those wherein

- a) Z, w, x, z and V are all zero;
- b) Z, w, V, and x are all zero, z is one, and L_2 is $\text{-C(O)-, -C(O)NH-, or -C(O)O-}$, most preferably -C(O)-O- , or -C(O)- with the carbonyl in each case attached to R_{16} or R_{17} ;
- c) Z, z and V are all zero, w and x are each one, R_6 is of formula IX wherein j, k, j1 and k1 are each zero, and D is one, and the aryl thereof is phenyl; and L_3 is -NHC(O)- with the nitrogen thereof attached to R_6 ;
- d) Z, w and x are zero, and V is one, A₁ is $\text{-CH}_2\text{CH}_2\text{O-}$ with the carbon thereof attached to L_4 , L_4 is -C(O)O- with the carbonyl thereof attached to R_{16} or R_{17} ;
- e) Z, V and x are zero, z and w are one, L_4 is -C(O)O- with the carbonyl attached to R_{15} or R_{17} , and R_6 being alkylene or hydroxy substituted alkylene of from 2-15 carbon atoms; and
- f) those groups of a) to e) above except that Z is one and wherein
 - i) M and T are one, G and Y are zero, R_9 is $C_2\text{-alkylene}$ or $C_2\text{-hydroxy substituted alkylene}$ and L_5 is -NHC(O)- with the nitrogen attached to R_6 ;
 - ii) M, G, Y and T are all one, R_9 is $C_2\text{-alkylene}$ or $C_2\text{-hydroxy substituted alkylene}$, L_5 is -NHC(O)O- with the oxygen bound to R_9 , R_6 is as defined above, preferably a divalent aliphatic or cycloaliphatic or arylene group and L_6 is -NHC(O)- with the nitrogen attached to R_6 ;
 - iii) M is zero, G, Y and T are all one and $L_5R_6L_6$ is $\text{-C(O)NH-R}_6\text{-NHC(O)-}$.

- 35 Even more highly preferred macromers of formulae I-III are those within formula Ia and IIa having each Cap independently selected from formulae VI and VII in which Z is zero to result in Cap₁ of the formulae $R_{15}(L_4)_z(R_6)_w(A_1)_v(L_3)_x$ (VIa) and



- 40 and macromers of the formula Cap₁-Grp₁-Cap₂ (IIIa).

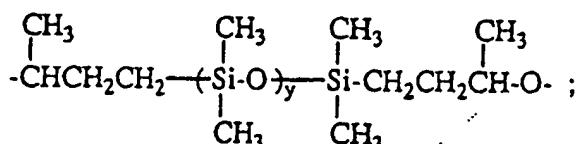
Very highly preferred macromers of formula IIIa have R_{16} in formula VIa selected from those of formula VIII wherein each of $R_{18}\text{-R}_{12}$ is independently hydrogen or methyl. Also preferred within this very highly preferred group are those wherein V is zero.

- 45 Highly preferred vinyl containing Cap groups terminating the macromer are acryl, methacryl, and styryl groups bound directly to or through an ethyloxy or oxyethyloxy to the balance of Cap or to the non-Cap portion of the macromer.

Specifically preferred embodiments of the present invention within formulae IIa and III include those wherein

50

Sil is



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a is one:

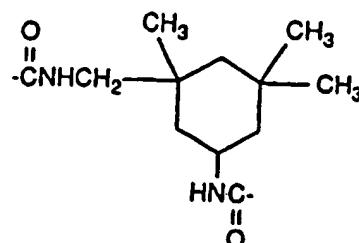
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e is zero;
R₁₄ and R₁₅ are each -O-;

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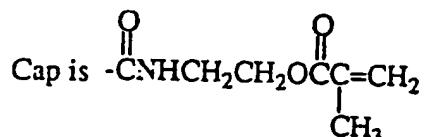
L is

10



15 h is one;
A is (CH₂CH₂O)_t; and
p is zero;
m is zero;

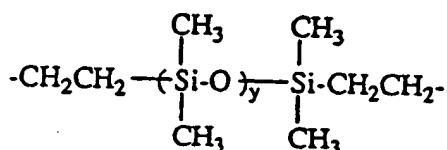
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25 Further preferred is a macromer of the formula
Cap-Sil-L-O-A-L-Sil-Cap

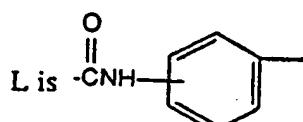
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wherein Sil is



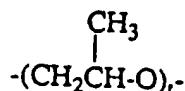
35 wherein y is 1 to 200, (especially y of about 4, 7, and about 16);

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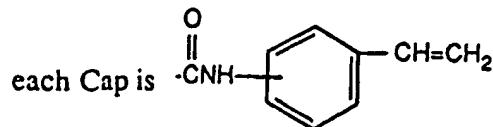


45 with the phenyl ring thereof bound to Sil,
m is zero to 3;
A is -(CH₂CH₂O)_t-,

50



wherein t is 3 to 200, or a poloxamer or reverse poloxamer having t polyoxyalkylene units per A group (especially t of about 6-8, about 45-55, and about 90-95); and



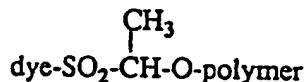
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- In the foregoing, all alkyl groups whether mentioned alone or as part of another group are preferably C₁-C₄ alkyl, such as methyl, ethyl, propyl and butyl, especially t-butyl, with the exception that adjacent groups on aryl rings cannot each be t-butyl. These alkyl groups may be straight chain or branched chain.
- 10 When the alkyl is a substituent on a phenyl ring, it is preferably attached at the para position. Preferably alkenyl groups, whether alone or as part of another group, are C₂-C₄ alkenyl, such as ethenyl, propenyl and butenyl. Preferred aryl groups (whether alone or as part of another group) are phenyl and naphthyl, more preferably phenyl. Preferably the aryl groups are still further substituted by C₁-C₄ alkyl, more preferably t-butyl, most preferably in the para position. Halogen may be chloro, bromo, iodo or fluoro.
- 15 Color may be added to the polymerized material or to the macromers via typical dying techniques. One such manner is by insuring hydroxy groups are introduced onto the macromer backbone or substituent thereof.
- Typical color groups useful in these embodiments include, but are not limited to, the hydroxy-reactive dyes known in the art under the tradename Remazol, manufactured by American Hoechst. Examples of the 20 Remazol dyes which are especially useful are:

Dye	Color Index Code
Remazol Brill Blue RW	Reactive Blue 19
Remazol Yellow GR	Reactive Yellow 15
Remazol Black B	Reactive Black 5
Remazol Golden Orange 3GA	Reactive Orange 78
Remazol Turquoise P	Reactive Blue 21

30

- all of which have at least one group of the formula
 $-\text{SO}_2\text{-CH}_2\text{CH}_2\text{O-SO}_3^{\ominus}$
 which reacts with the polymer or monomer hydroxy group to yield a
 35 dye-SO₂-CH₂-CH₂-O-polymer or



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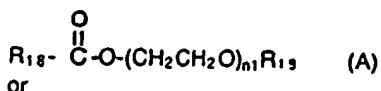
group, preferably the former. In such a manner, both excess free hydroxy groups are disposed of and colored contact lenses can be realized simultaneously.

- If the polymerized macromers set forth above have inherently too low a water content, i.e. below 10 % water content, the polymer is not within this invention. However, the macromers can be copolymerized with a hydrophilic modifier so as to increase the water content to be within the instant invention. Whether the hydrophilic modifier is needed or not, and the amount which is needed, is dependent upon the desired polymer water content. Preferably, when the hydrophilic modifier is present, in accordance with the above, it is present in an amount of up to about 50 % by weight preferably about 1 % to about 30 %, more preferably about 5 % to about 25 %, still more preferably about 10 % to about 15 % of the resultant polymer.

In addition to the hydrophilic modifier, other comonomers which may be present in the polymer are monomers coreactive with the monomer of formula I. Such additional monomers may be present in a minor amount of up to about 20 % by weight of the resultant polymer. When such comonomers are excessively hydrophobic, additional hydrophilic modifier may be incorporated so as to achieve the appropriate water content.

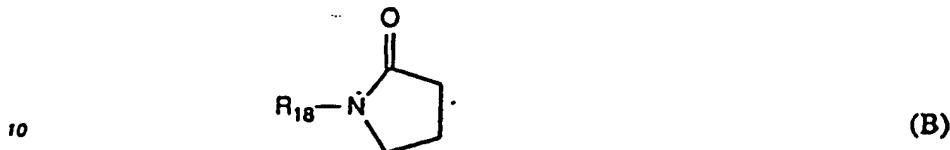
The hydrophilic modifier is a monomer which is coreactive with a monomer of formula I and is typically selected from

aa) polyethyleneglycols of the formula



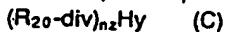
ab) pyrrolidones of the formula

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wherein R_{19} is hydrogen or $\text{C}_1\text{-C}_7$ alkyl, preferably $\text{C}_1\text{-C}_4$ alkyl, $n1$ is an integer of from 1 - 25, or

15 ac) a compound of the formula



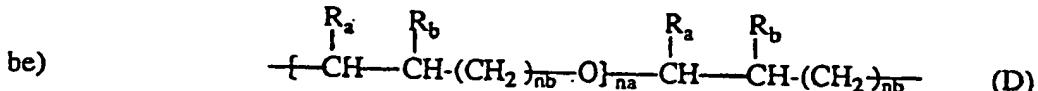
wherein R_{18} is a polymerizable or reactive moiety selected from i) ethylenically unsaturated radicals, preferably vinyl, 1-methylvinyl, 2-methylvinyl, or allyl, ii) anhydrides, iii) amides, iv) acids, v) esters, vi) ethers, vii) amine halides, R_{20} is selected from the meanings given for R_{18} and ix) epoxy groups, especially glycidyl, x) isocyanates and isothiocyanates and xi) hydroxy; div is selected from

20 ba) a divalent aliphatic group of up to 25 carbon atoms, preferably alkyl, alkenyl or alkynyl, which may also be interrupted, or terminated, or interrupted and terminated by oxy, carbonyloxy, amino, aminocarbonyl, oxycarbonyl, ureido, oxycarbonylamino, or carbonylamino;
 bb) a divalent 5 - 7 membered cycloaliphatic or 5 - 7 membered cycloaliphatic- $\text{C}_1\text{-C}_{20}$ -aliphatic group which may also be interrupted, terminated, or interrupted and terminated as in group ba) above except that said interruptions cannot occur within said cycloaliphatic portions;

25 bc) a divalent arylene group having 6-25 carbon atoms which is unsubstituted or substituted by at least one substituent selected from halogen, $\text{C}_1\text{-C}_4$ alkyl, and $\text{C}_1\text{-C}_{12}$ perhaloalkyl;

30 bd) a divalent aralkyl or alkaryl or -alkylene-aryl-alkylene- having 7 - 25 carbon atoms which is uninterrupted or interrupted in the alkyl portion, or terminated, or interrupted in the alkyl portion and terminated with an interrupting or terminating group as mentioned in ba) above, and each of said uninterrupted, interrupted, and terminated aralkyl and alkaryl groups is further unsubstituted or substituted by a substituent selected from halogen, $\text{C}_1\text{-C}_4$ alkyl, and $\text{C}_1\text{-C}_{12}$ perhaloalkyl;

35



40 wherein na is an integer of 8-100; and

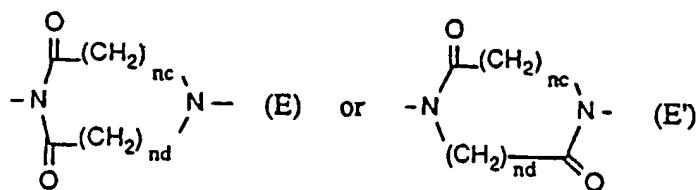
bea) R_a is hydrogen, R_b is methyl, and nb is zero; or

beb) R_a is methyl, R_b is hydrogen, and nb is zero; or

bec) R_a and R_b are hydrogen and nb is one; nz is an integer of 1 up to the valence of Hy and where nz is less than the valence of Hy , the remaining valences of Hy are taken up with hydrogens; and Hy is a hydrophilic group selected from

45 ca) morpholino; cyclic amide radicals of 5 - 7 ring members; saturated and unsaturated cyclic N,N-diamide radicals of 5 - 6 ring members; groups of the formula

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having 6 - 7 ring members wherein nc and nd are selected from 0 - 2; and cyclic amines of 5 - 6 ring members; each unsubstituted or substituted by hydroxy- $\text{C}_1\text{-C}_5$ alkyl, carboxy, or lower alkyl;

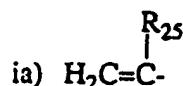
cb) tetrahydrofurfuryl;

cc) mono-, di-, and polysaccharide radicals, whether straight chain or cyclic, their corresponding sugar alcohol radicals, pentaerythritol radicals, and polyvinyl alcohol radicals; and

5 cd) polyhydroxy C₂-C₇ alkyl radicals; and said reactive group R₁₈ is capable of reacting with one or more sites in said formula III.

Preferably the hydrophilic modifier has R₂₀ selected from

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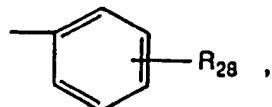


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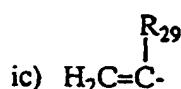
and the terminus of div to which it is bound is -C(O)R₂₅, the carbonyl being bound to R₁₈, where R₂₅ is hydrogen or methyl and R₂₆ is -O-, or -NR₂₇- with R₂₇ being hydrogen or lower alkyl;

ib) H₂C=CH- and the terminus of div to which it is bound is

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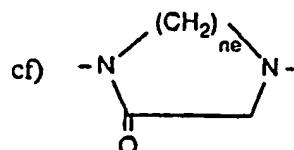
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and the terminus of div to which it is bound is -C(O)R₃₀-, the carbonyl being bound to R₂₀ wherein R₃₀ is lower alkylene or -[CH₂CH(loweralkyl)-O]-, and R₂₉ is hydrogen, lower alkyl, or cyano; and has Hy selected from

ce) morpholino which is unsubstituted or mono- up to tetra-substituted by lower alkyl, preferably methyl or ethyl;

35

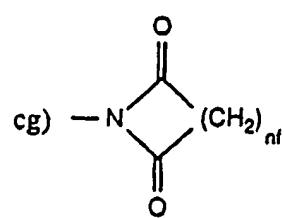
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wherein n is one, two, or three, preferably 1, each of which is unsubstituted or substituted, preferably mono- or disubstituted, by lower alkyl, preferably methyl or ethyl;

45

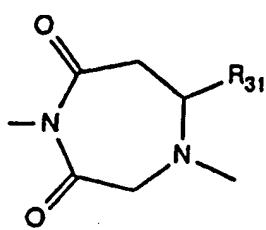
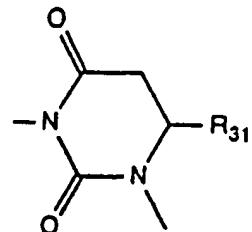
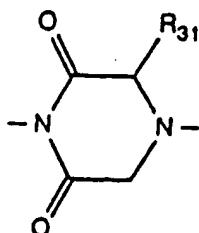
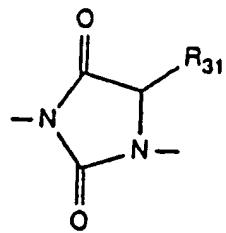
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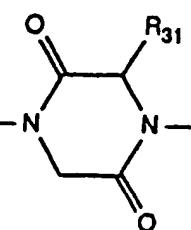
55 where n is 2 or 3, preferably 2,

each of which is unsubstituted or substituted by lower alkyl, preferably methyl or ethyl;

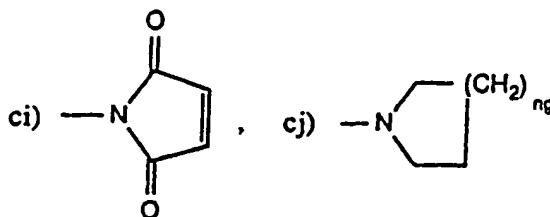
ch) a divalent group of the formula



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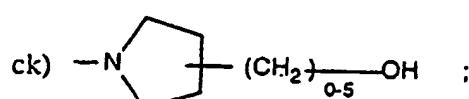


20 wherein R₃ is hydrogen or carboxy;

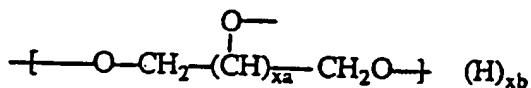


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where n_g is one or two,
each of which is unsubstituted or substituted by lower alkyl, preferably methyl or ethyl.



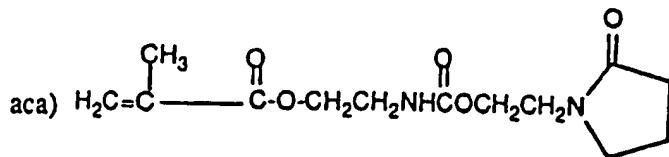
40 c) a polyol selected from polyvinyl alcohol radicals.



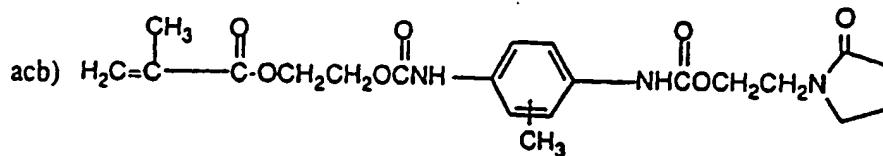
wherein x_a is 2 - 10, preferably 3 - 4, and x_b is an integer from zero, preferably at least 0.5 times x_a up to $x_a + 1$ inclusive, the cyclic saccharide analogs thereof, the di-tetra saccharides thereof, preferably having saccharide-saccharide links between the 1 and 4 carbon positions thereof, preferably β -linkages, $C(CH_2O)_x \cdot (H)_{x_c}$ wherein x_c is 0 - 3, and polyhydroxy lower alkylene glycol radicals wherein up to 50 %, preferably up to 25 %, more preferably up to 10 %, of the hydroxy groups are missing their alcoholic hydrogens.

50 Most preferably the hydrophilic modifier of formula (C) is selected from

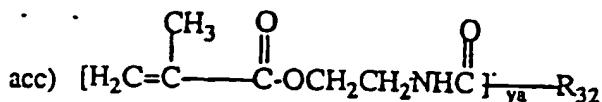
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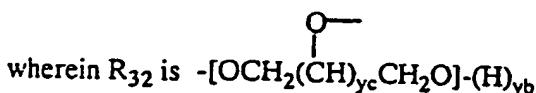
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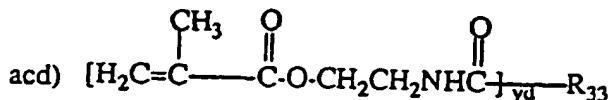
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in which y_c is 1-6, preferably 3-4 and y_b is 0 up to $(y_c + 1)$, preferably $(y_c - 1)$ to $(y_c + 1)$, more preferably y_c to $(y_c + 1)$, and y_a is 1 up to $(y_c + 2 - y_b)$,

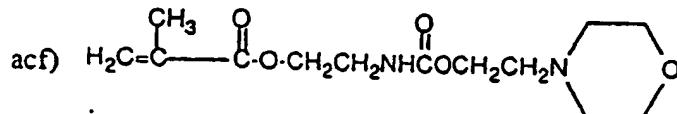
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wherein R_{33} is $\text{C}(\text{CH}_2\text{O})_c(\text{H})_{4-y_d}$ and y_d is 1 - 4, preferably 1 - 2;

ace) polyvinyl alcohol having at least one and up to 50 % preferably 25 %, more preferably 10 %, inclusive, of the alcoholic hydrogens thereof absent;

40



Preferably, when Cap is a vinyl containing group or one or more of the aforementioned R groups within formulas I-III contain an ethylenically unsaturated group, then the macromer can be crosslinked in the presence of a vinylic group containing hydrophilic modifier and/or vinylic group containing crosslinking agents. The instant macromer can be crosslinked in the presence or absence of up to less than about 50 %, preferably up to about 30 %, most preferably up to about 10 % by weight of vinylically unsaturated hydrophilic modifiers and/or other vinylic comonomers.

When Cap does not have a vinylic group, but takes part in crosslinking, Cap is of formula VII. Crosslinking is then typically carried out by condensation with a tri- or polyfunctional coreactive monomer. For example, when Cap terminates in OH, then the coreactive monomer functional group can be -COOH, OCN, SCN, -NH₂, -NH(alkyl) etc.; when Cap terminates in -NH₂ or -NH(alkyl), the reactive comonomer functional group can be a conventional acyl leaving group; and when Cap terminates in OCN- or SCN-, then the reactive comonomer functional group can be OH. Similarly, the other coreactive functional groups mentioned in terms of either Cap or the coreactive monomer can be interchanged.

Suitable vinylic monomers and coreactive monomers for condensation are set forth below. However, the list is not exhaustive and those of ordinary skill will appreciate the modifications, additions, and alternatives which may also be employed.

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However, the degree of crosslinking in the finished crosslinked polymer should not exceed 20 %, preferably not greater than 10 %, more preferably not greater than 5 %, still more preferably 1-4 %, most preferably 2-3 %.

- 5 A highly preferred embodiment within the polymers fabricated from macromers of formula I, requires that not more than 20-70 %, preferably not more than 50 % of the A groups are polyethylene glycol. In another highly preferred group A is homopolymeric polyethylene oxide or polypropylene oxide.

The number of A units and the chain length and nature of the substituents on the polyoxyethylene segment is determined by the degree of wettability desired in the polymer or the compound of formula I. In general, the polymer should be sufficiently hydrophilic in its surface properties such that the polymer 10 exhibits a contact angle with distilled water at 20°C of less than 60°, preferably less than 40°, more preferably less than 25°, still more preferably less than 15°, most preferably less than 10°.

The greater the number of siloxane units, the greater the number of oxyalkylene units is generally required to reduce the contact angle to within the above limits.

As water is taken up, the oxygen permeability of the polymers tends to be reduced. However, with the 15 water content and swellability increased due to hydrophilic modifier the drop in Dk over the low water content analogs is surprisingly less drastic than would otherwise be expected. Advantageously, the instant polymers absorb at least 10 % by weight water, preferably 15 - 90 % by weight, more preferably 20 - 85 % by weight, still more preferably 25 - 75 % by weight, most preferably 35 - 55 % by weight water.

20 Highly preferred are those polymers which exhibit a contact angle of less than 25°, more preferably less than 15° and most preferably less than 10°.

The reactive vinylic macromers of the invention can characteristically be polymerized to form crosslinked polymers under conventional polymerization conditions.

If desired, the monomer reaction mixture may contain a catalytic amount of a conventional polymerization catalyst, preferably a free radical catalyst. Of particular interest are conventional peroxide and azo 25 catalysts, such as hydrogen peroxide, benzoyl peroxide, tert-butyl peroctoate, benzoyl peroxide or azobisisobutyronitrile.

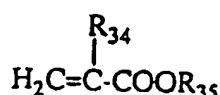
The polymerization can generally be carried out at temperatures between about 20° and about 150°C, for a period between about 1 and about 24 hours. It is understood that the time and temperature in such a 30 reaction are inversely related. Thus, temperatures employed in the upper end of the temperature range will generally provide reaction times near the lower end of the time range. Preferably, the polymerization is conducted in the presence of actinic radiation, such as UV light.

Depending upon the nature of the polymer mixture, it may be desirable for the polymers obtained from such polymerizations to be post cured, e.g. at a somewhat elevated temperature such as between about 60°C and about 150°C.

35 For the preparation of contact lenses, the polymer mixture may be cast directly in the shape of the lens, or the polymerization may be carried out in a mold having a shape convenient for further processing, such as in the shape of small cylinders or "buttons", which can then be machined.

Minor amounts i.e. less than 50 %, preferably up to 30 %, and most preferably up to no more than 40 about 10 % by weight, of conventional copolymerizable vinyl monomers other than hydrophilic modifiers, can be employed as extenders or the like, in the preparation of the instant polymer, as copolymer constituents. However, if the total hydrophilic modifier content is within the foregoing limits, the hydrophilic modifiers can also be used as such extenders. Suitable vinyl monomers include: acrylates and methacrylates of the general formula

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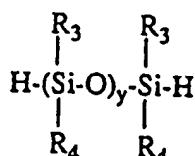
50 where R₃₄ is hydrogen or methyl and R₃₅ is a straight chain or branched aliphatic, cycloaliphatic or aromatic group having up to 20 carbon atoms which is unsubstituted or substituted by one or more alkoxy, alkanoyloxy or alkyl of up to 12 carbon atoms, or by halo, especially chloro or preferably fluoro, or C₃-C₈ polyalkyleneoxy of 2 to about 100 units; acrylamides and methacrylamides of the general formula

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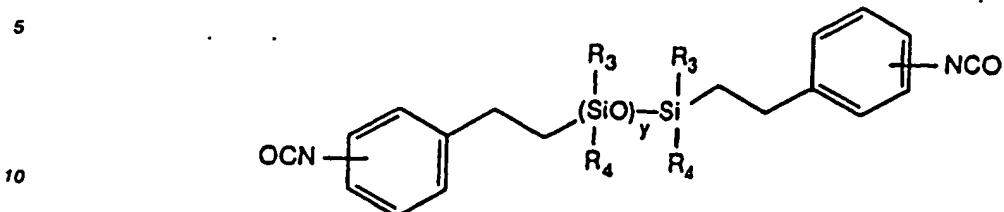


- where R_{34} and R_{35} are as defined above; vinyl ethers of the formula
 $H_2C = CH-O-R_{35}$
 where R_{35} is as defined above; vinyl esters of the formula
 $H_2C = CH-OOC-R_{35}$
- 5 where R_{35} is as defined above;
 maleates and fumarates of the formula
 $R_{35}OOC-HC = CH-COOR_{35}$
 where R_{35} is as defined above;
 and vinylic substituted hydrocarbons of the formula
- 10 $R_{34}CH = CHR_{35}$
 where R_{34} and R_{35} are as defined above.
- Useful monomers include, for example:
 methyl-, ethyl-, propyl-, isopropyl-, butyl-, ethoxyethyl-, methoxyethyl-, ethoxypropyl-, phenyl-, benzyl-, cyclohexyl-, hexafluoroisopropyl-, or n-octyl-acrylates and -methacrylates as well as the corresponding
 15 acrylamides and methacrylamides; dimethylfumarate, dimethylmaleate, diethylfumarate, methyl vinyl ether, ethoxyethyl vinyl ether, vinyl acetate, vinyl propionate, vinyl benzoate, acrylonitrile, styrene, alpha-methyl styrene, 1-hexene, vinyl chloride, vinyl methyl ketone, vinyl stearate, 2-hexene and 2-ethylhexyl methacrylate.
- In one preferred aspect, the instant polymers are free from copolymer units of such conventional
 20 monomers which are not hydrophilic modifiers.
- The vinylic monomers of formulae I-III can be prepared by methods known, per se.
 For example, the siloxane/polyalkylene oxide containing divinylic monomers of formulae I-III may be prepared by reacting a siloxane diol of the formula $HO-Sil-H$, wherein Sil is a group of formula IV, as defined hereinbefore, with a sufficient amount of a difunctional reactive group containing compound at least
 25 one of which reactive groups is coreactive with OH, such as isocyanate; activated carboxy, such as an anhydride, an acid halide or a carboxy ester, or is a leaving group, such as a halide, sulfato or the like, to form the corresponding reactive group containing endcapped derivative. Such reactive compounds for forming preferred macromers include toluene diisocyanate, isophorone diisocyanate, and polyalkylene oxide mono- or di-capped by isocyanate.
- 30 The resulting endcapped siloxane derivative can then be reacted with a polyoxyalkylene diol of the formula $HO-(A)-H$, wherein -A- is a group of formula V above to form the corresponding polyoxyalkylene - siloxane - polyoxyalkylene diol. This diol can be then reacted with a reactive end Cap group containing
 35 -L- to form the corresponding di-functional reactive group containing compound having the group -L- to further sequentially react with a further difunctional reactive group containing compound having the group siloxane of the formula $HO-Sil-H$. One may continue building up alternative polyoxyalkylene/siloxane unit containing diols in this manner, as desired. Then this diol may be endcapped with a reactive group
 40 containing vinylic monomer having a terminal 'Cap' moiety or the diol reacted with a sufficient amount of difunctional reactive group containing compound to endcap the diol with a reactive group, such as e.g. an isocyanate, etc. group which is then reacted with the appropriate 'Cap' containing compound, such as a vinylic amine or alcohol, or other copolymerizable monomer having a crosslinkable group to obtain the corresponding product of formula III.
- 45 Of course, instead of starting with a siloxane of the formula $HO-Sil-H$ and building up the alternating sequence therefrom, one may instead begin with a polyoxyalkylene diol of the formula $HO-(A)-H$ and, after endcapping the same with difunctional reactive groups, condense the same with the siloxane until the desired number alternating siloxane/poly alkylene oxide groups is attained and terminate the diol with Cap groups as described above.
- 50 Alternative synthesis of the direactive siloxane can be accomplished with a siloxane dihydride of the formula

55



and reacting it (as known in the art) with a vinyl containing compound containing another reactive group, typically a hydroxy reactive group, such as styrene isocyanate, to yield the dicapped siloxane, such as



Such reactive group capped siloxane may then be used in the same manner as the reactive endcapped HO-Sil-H indicated above.

15 Synthesis of the macromers may be accomplished neat or in solvents as indicated in the examples attached hereto in accordance with known synthetic techniques.

The above reactive monomers are characteristically polymerized under conventional polymerization conditions with a hydrophilic modifier of formulae A-C or a mixture of a hydrophilic modifier of formulae A-C and a copolymerizable monomer. In those vinylic macromers containing but one vinyl group, a minor amount e.g. from about 0.01 to about 5 weight percent, based on the macromer of formula I-III, of a conventional crosslinking agent, may be employed. Suitable crosslinking agents include diolefinic monomers such as:

20 Allyl acrylate and methacrylate, alkylene glycol and polyalkylene glycol diacrylates and dimethacrylates, such as ethyleneglycol dimethacrylate, diethylene glycol dimethacrylate, and propylene glycol dimethacrylate; trimethylol propane triacrylate; pentaerythritol tetraacrylate, divinylbenzene; divinyl ether; divinyl sulfone; bisphenol A diacrylate or dimethacrylate; methylene bisacrylamide; diallyl phthalate; triallyl melamine and hexamethylene diacrylate and dimethacrylate. Also, such minor amounts of a crosslinking agent may be employed, if desired, in the polymerization of the di-vinyl monomer of formula I, II or III.

25 When the macromers of formula I-III have free hydroxy, isocyanato, carboxylic or amine groups, suitable crosslinking agents contain di- or polyfunctional co-reactive groups to form addition or condensation reactions linking 2 or more chains.

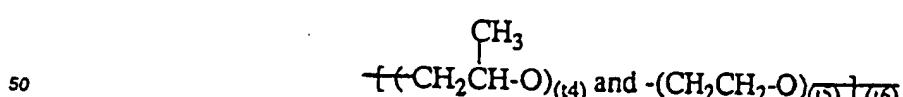
30 If desired, the macromer reaction mixture may contain a catalytic amount of a conventional catalyst, preferably a free radical catalyst. Of particular interest are conventional peroxide and azo catalysts, such as hydrogen peroxide, benzoyl peroxide, tert-butyl, peroctoate, benzoyl peroxide or azobis (isobutyronitrile).

35 The aforementioned reactions are generally straight forward additions or condensations and are typically conducted at a reaction temperature between about -10 °C and about 100 °C, depending upon the relative reactivity of the species involved, in the presence or absence of an inert diluent and in the optional presence of an addition or condensation catalyst if desired or appropriate. For reactions involving an isocyanate or acid halide, with a diol, for example, suitable optional catalysts include pyridine and triethylamine.

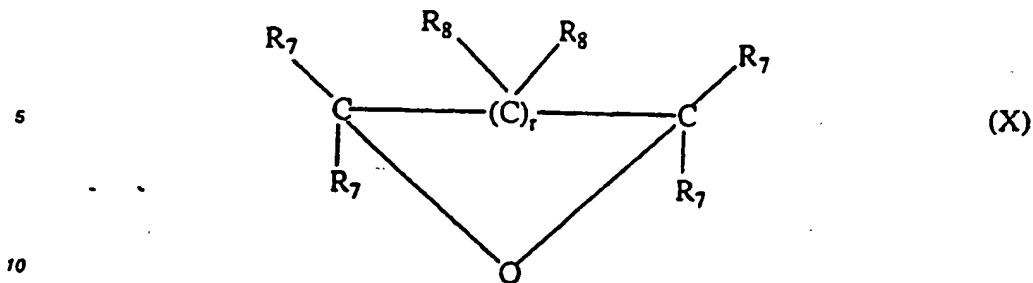
40 The siloxanes of the formula HO-Sil-H are known in the art and many are commercially readily available.

Also, the polyoxyalkylene diols of the formula HO-A-H are known or can be prepared by known methods.

45 Thus, the polyols of the formula HO-A-H are generally prepared by the addition reaction of t moles of an epoxide of formula X, or, assuming that A is a block copolymer of



(especially when $(t_4) + (t_5)](t_6)$ = about 30-70) of (t_4) time (t_5) moles of an epoxide of the formula



with (*t_s*) times (*t_c*) of a different epoxide of formula X, where R₇, R₈, r, t, (*t_s*), (*t_c*) are as defined above, optionally in the presence of a conventional alkylation catalyst, at atmospheric to elevated pressures of up to about 3000 kPa gauge, at temperatures between 0 °C and about 130 °C, optionally in the presence of an inert diluent. If desired, one may add to the reaction mixture, prior to the reaction of the epoxides, an aliphatic, aromatic or cycloaliphatic alcohol, acid or amine having up to 14 carbon atoms to prepare the corresponding mono-ols.

The reaction between the epoxides, when mixtures of different epoxides are employed to obtain the polyol of the formula HO-A-H, can be conducted by admixing the epoxides to obtain random copolymers or terpolymers, etc., or the addition can be conducted sequentially to form block copolymers having terminal hydroxy groups. Suitable catalysts include alkaline earth oxides, alkaline earth carbonates, alkyl zinc compounds, aluminum alkoxides, hydrates of ferric chloride, bromide and acetate, and gamma radiation. The reaction may also be initiated by the presence of a glycol, such as ethylene glycol or propylene glycol or by a polyol of higher functionality such as sucrose, or by an amine, such as ethylene diamine, toluenediamine, and so forth. Generally the length of time of the reaction will depend in part on the alkylene oxide employed, but can generally be from less than one to several score hours. Thus, ethylene oxide generally is about three times as active as propylene oxide, which in turn reacts more rapidly than 1,2-butylene oxide. The preparation of polyoxetanes and polytetrahydrofurans is generally initiated via ring opening oxonium formation using trialkyloxonium salts, carboxonium salts, acylium salts and the like.

Suitable diols of the formula HO-A-H include those prepared from epoxides such as: 1,2-propylene oxide; 1,2-butylene oxide; 1,2-epoxydecane; 1,2-epoxydodecane; 1,2-epoxyoctane; 2,3-epoxynorbornane; 1,2-epoxy-3-ethoxypropane; 1,2-epoxy-3-phenoxypropane; 2,3-epoxypropyl 4-methoxyphenyl ether; tetrahydrofuran; 1,2-epoxy-3-cyclohexyloxypropane; oxetane; 1,2-epoxy-5-hexene; 1,2-epoxyethylbenzene; 1,2-epoxy-1-methoxy-2-methylpropane; perfluorohexylethoxypropylene oxide; benzyl oxypropylene oxide, and the like. Also, the aforementioned epoxides may be employed as mixtures thereof. Further, certain cyclic ethers of formula X where r is 3 and the carbocyclic portion of the ring is substituted are resistant to polymerization alone, but copolymerize quite readily with more reactive cyclic ethers. Suitable comonomers include, for example, 2-methyl-tetrahydrofuran and 3-methyl-tetrahydrofuran. Also, while ethylene oxide may be employed as a co-monomer, ethylene oxide polymers, in the absence of more hydrophobic units, is characteristically too hydrophilic and absorbs too much aqueous fluid to be of use in accordance with the instant invention. However, ethylene oxide/propylene oxide copolymeric diols wherein there is 30-80 %, preferably greater than 50 %, more preferably greater than 66 % propylene oxide, on a mole basis, is sufficiently hydrophobic so as to be substantially non-swellable in aqueous media, and yet sufficiently hydrophilic so as to exhibit a contact angle with water of less than 60°; preferably less than 40°, more preferably less than 25°, more preferably less than 15°, most preferably less than 10°.

Many polymer diols of the formula HO-A-H are commercially available. Thus, suitable diol products include poloxamers having the general formula HO(CH₂CH₂O)_a-(CH(CH₃)CH₂O)_b-(CH₂CH₂O)_c-H wherein b' has a value between about 16 and 100 and the sum of a' and c' is between about 4 and about 100. While each of the following poloxamers is beyond the current definition of the preferable A groups, they may be used to form the non-referable A groups within any one macromer. For example, if 30 % of the A groups in a macromer are poloxamers of (a') = 5, (b') = 15, (c') = 5, then the remainder of the A groups in that macromer may be any of the poloxamers set forth below. Examples of such poloxamers and their average values of a', b' and c' include poloxamer 101 (a' is 2, b' is 16, c' is 2); poloxamer 122 (a' is 5, b' is 21, c' is 5); poloxamer 181 (a' is 3, b' is 30, c' is 3); poloxamer 212 (a' is 8, b' is 35, c' is 8); poloxamer 231 (a' is 6, b' is 39, c' is 6); poloxamer 282 (a' is 10, b' is 47, c' is 10); poloxamer 333 (a' is 7, b' is 54, c' is 7); poloxamer 401 (a' is 6, b' is 67, c' is 6).

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Such poloxamers are available, e.g. from BASF Wyandotte under their Pluronic® brand name. Also suitable are the "reverse poloxamers", having polyethylene glycol bounded on each side by polypropylene glycol.

5 Polypropylene ether glycols include commercially available products having a molecular weight range between about 400 and about 4,000.

The hydrophilic modifiers can be prepared as disclosed in EP-A-331633, entitled HYDROPHILIC MODIFIER MONOMERS, invented by Frank Molock and Richard Robertson.

10 Typically, conventionally fully swollen polyhydroxyethyl methacrylate lenses which are sparingly cross-linked possess a $Dk(x10^{-10})$, ($\text{mm}^3 \cdot \text{ml O}_2/\text{cm}^2 \cdot \text{sec} \cdot \text{mmHg}$) value of about 5-7.

15 The instant polymers for use as an ophthalmic device, such as a contact lens, possess a $Dk(x10^{-10})$ value generally greater than 7 - 10, preferably greater than about 15, more preferably greater than about 20 and still more preferably greater than about 40, yet more preferably greater than 80, even more preferably greater than 100, most preferably at least 150.

15 The following examples are for illustrative purposes and are not to be construed as limiting the invention. All parts are by weight unless otherwise specified.

In the examples the following test methods were used in evaluating the polymer films:

a) Oxygen permeability (Dk) is determined from measurements on a Schema Versatae or Createch polarographic cell.

20 b) Wettability or lubricity is evaluated by a feel comparison to crosslinked polyHEMA (i.e. polymerized 2-hydroxyethyl methacrylate + 1 % ethylene glycol dimethacrylate). The surface lubricity of polyHEMA is designated (B); more wettable than polyHEMA is designated (A) and a less wettable surface than polyHEMA is designated (C).

c) Tensile strength is qualitatively evaluated by pulling on a sheet of the material by hand and then comparing the result to a material previously evaluated by a micromechanical tester to be 14 kg/cm^2 . A 25 measurement found to be similar to this "standard" is designated (2); a higher value is designated (1); a lower value is designated (3); while a much lower value is designated (4).

Example 1:

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This example illustrates the sequential synthesis of a polydimethyl-siloxane/polyether urethane-linked adduct, $Z_1 \cdot \{\text{IPDI-PEG-IEM}\}_2$, where Z_1 is a polydimethyl siloxane, IPDI is isophorone diisocyanate, PEG is a polyethylene glycol and IEM is isocyanatoethyl methacrylate; and, the solution polymerization of this adduct.

35

Synthesis of $Z_1 \cdot \{\text{IPDI-PEG-IEM}\}_2$, Diadduct:

A stock solution of $Z_1 \cdot \{\text{IPDI}\}_2$ is first formed by combining 8.0054 g (0.0036 mole) Shin-Etsu X-61-504A (1000) (MW = 2212) with 1.6010 g (0.0072 mole) IPDI and 1 microliter of dibutyltin dilaurate (DBTL) and then stirring overnight at room temperature. The percentage of isocyanate reacted (generally 48-50 %) is determined by dibutylamine titration and varies with the precise value of Z_1 molecular weight actually used. Then, a calculated molar amount of PEG is dissolved in solvent and the corresponding amount of the $Z_1 \cdot \{\text{IPDI}\}_2$ stock solution is added to form $Z_1 \cdot \{\text{IPDI-PEG}\}_2$. The solution is reacted at 50 °C with stirring overnight. IR verifies complete reaction of the isocyanate functionality (disappearance of absorption at 2270 cm^{-1}).

The calculated molar amount of IEM is added to a solution $Z_1 \cdot \{\text{IPDI-PEG}\}_2$ and reacted at room temperature overnight with stirring.

50

Polymerization of Diadduct; Hydrogel Formation:

The $Z_1 \cdot \{\text{IPDI-PEG-IEM}\}_2$ adduct in solvent is mixed with initiator (benzoin methyl ether, BME) poured into flat "sandwich" molds and polymerized with UV light (Sylvania, Blacklight Blue, 15 W) at room temperature for 3 hours. The polymerized films are removed from the molds, extracted in water several times, heated in boiling water for 10 minutes and then allowed to equilibrate in room temperature water (generally overnight).

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Example 2:

This example shows the resultant water contents and oxygen permeability values of polydimethyl siloxane:PEG hydrogels, i.e. crosslinked Z₁{IPDI-PEG-IEM)₂, solution polymerized using different molecular weights of PEG (200, 400, 600, 900, 1000, 1500, and 2000). Different solvents are used as indicated below to achieve solubility of the diadduct. Films are prepared as in example 1 except for samples 1, 2 and 3 in which PEG and Z₁{IPdi)₂ are reacted at room temperature and samples 6 and 7 in which PEG and Z₁{IPDI)₂ are reacted at 50 °C in the presence of additional dibutyltin dilaurate catalyst.

Sample	Wt.% in the Polymerization Mixture					
	Z·	IPDI	PEG (MW)	IEM	Solvent	BME
1	34.4	6.9	6.1 (200)	4.9	47.7 (1)	0.18
2	28.0	5.6	10.9-(400)	4.2	51.2 (2)	0.12
3	27.5	5.5	15.0 (600)	3.8	48.1 (2)	0.11
4	24.1	4.8	19.5 (900)	3.5	48.1 (1)	0.10
5	23.0	4.6	20.7 (1000)	3.2	48.5 (1)	0.14
6	18.8	3.8	25.5 (1500)	2.7	49.3 (3)	0.10
7	16.6	3.3	29.6 (2000)	2.4	48.0 (3)	0.49

solvents:(1) = isopropyl acetate. (2) = dichloromethane. (3) = acetone

Sample	Physical Properties of Hydrogel			
	% H ₂ O Content	Clarity	Wettability	DK (barrier)
1	5.6	Clear	C	-
2	16.6	Clear	B	70.2
3	27.9	Clear	B	-
4	39.8	Clear	A	66.1
5	46.0	Clear	A	59.5
6	57.9	Sl. Hazy	A	45.2
7	79.0	Opaque	A	47.5

35

As shown above water content increases with higher molecular weight PEG. Oxygen permeability however, decreases with the higher molecular weight PEG.

40 Example 3:

This example illustrates how the clarity of polydimethyl siloxane/PEG hydrogels is affected by varying the proportion of solvent. Films are made as in example 1 except that the molecular weight of PEG is 1000 and the solvent used is isopropyl acetate (IPAC). Samples 6 and 8 are made as in example 1 with 50 % IPAC and are subsequently diluted to 60 and 75 % IPAC respectively prior to the addition of BME and UV irradiation. Samples 1 and 2 do not contain enough solvent to dissolve the reactants and, therefore, the synthesis is stopped prior to IEM addition and films are not made.

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Sample	Wt.% In the Polymerization Mixture						Clarity
	Z ₁	IPDI	PEG	IEM	Solvent	BME	
5	1	37.7	7.6	34.1	-	20.56	-
	2	37.0	7.4	33.4	-	22.19	-
	3	31.8	6.4	28.5	4.4	28.91	0.54
	4	26.7	5.4	24.2	3.8	40.04	0.50
	5	23.0	4.6	20.7	3.2	48.45	0.14
	6	17.8	3.6	16.0	2.5	60.18	0.20
	7	15.2	3.0	13.7	2.2	65.99	0.12
	8	11.1	2.2	10.0	1.5	75.07	0.18

15 As shown above clarity increases with increased solvent concentration.

Example 4:

20 This example shows the effect of comonomer addition of the physical properties of Z₁ PEG hydrogel films. Films are made as in example 3 (sample 5) except that a comonomer (N,N-dimethyl acrylamide, DMA; N-vinyl pyrrolidone, NVP; 2-hydroxyethyl methacrylate, HEMA; or methyl methacrylate, MMA) is added just prior to the addition of initiator.

Sample	Wt.% In the Polymerization Mixture							% H ₂ O Content in Hydrogel
	Z ₁	IPDI	PEG	IEM	IPAC	Comonomer	BME	
30	1	21.8	4.4	19.7	3.0	45.9	5.2 MMA	0.10
	2	23.0	4.6	20.7	3.2	48.5	0	0.14
	3	21.5	4.3	19.3	2.9	45.2	6.7 DMA	0.13
	4	21.8	4.4	19.6	3.0	45.8	5.5 NVP	0.15
	5	21.8	4.4	19.7	3.0	45.9	5.2 HEMA	0.13

35 MMA = methylmethacrylate;
DMA = N,N-dimethylacrylamide;
NVP = N-vinylpyrrolidone;
HEMA = 2-hydroxyethyl methacrylate.

40 As shown above, addition of comonomers has little effect on wettability or clarity. All hydrogels are clear and have an A-wettability.

Example 5:

45 This example compares the physical properties of Z₁/PEG hydrogel films made by combining PEG MW 1000 with lower molecular weight PEGs (200, 400 and 600) in various ratios. Except for sample 6, films are prepared as described in example 1 using isopropyl acetate (IPAC) as solvent and combining the molecular weight PEGs indicated below. Sample 6 is prepared by separately synthesis of Z₁/PEG 400 and Z₁/PEG 1000 according to example 1 using isopropyl acetate as solvent and then combining them prior to the addition of Initiator and UV irradiation.

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Sample	Mole Ratio	Wt % in the Polymerization Mixture						
		Z-	IPDI	PEG (MW)	IEM	IPAC	BME	
5	Low MW PEG:PEG 1000							
	1	0.1	23.0	4.6	20.7 (1000)	3.2	48.5	0.14
	2	PEG 400:PEG 1000 1:7	24.3	4.8	0.5 (200) 19.2 (1000)	3.5	47.6	0.13
	3	PEG 400:PEG 1000 1:9	23.8	4.7	0.8 (400) 19.3 (1000)	3.3	48.0	0.14
	4	PEG 400:PEG 1000 1:3	24.2	4.9	2.2 (400) 16.5 (1000)	3.4	48.8	0.14
	5	PEG 400:PEG 1000 1:1.5	25.5	5.1	3.7 (400) 13.8 (1000)	3.7	48.2	0.16
	6	PEG 400:PEG 1000 1:1.5	25.7	5.1	3.7 (400) 12.9 (1000)	3.6	49.0	0.13
10	7	PEG 600:PEG 1000 1:3	24.0	4.8	3.3 (600) 16.2 (1000)	3.4	48.3	0.18
20	Sample	Physical Properties of Hydrogel						
	% H ₂ O Content	Clarity	Wettability	Strength				
	1	45.4	Clear	A				
	2	39.9	Clear	A				
	3	41.5	Clear	A				
	4	38.2	Clear	A				
25	5	33.4	Clear	A				
	6	39.8	Clear	A				
	7	38.5	Clear	A				

30

The results show that incorporation of low molecular weight PEGs decreases water content but maintains clarity and wettability of the resultant films.

35 Example 6:

This example demonstrates the effect of initiator level on the physical properties of Z- PEG hydrogel films with similar compositions. The films are prepared as described in example 3 (sample 5).

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	Sample	Wt.% In the Polymerization Mixture					
		Z ₁	IPDI	PEG	IEM	IPAC	BME
5	1	23.0	4.6	20.8	3.2	48.4	0.04
	2	22.9	4.6	20.7	3.2	48.6	0.08
	3	23.1	4.6	20.7	3.1	48.4	0.12
	4	23.0	4.6	20.7	3.2	48.5	0.14
	5	23.0	4.6	20.8	3.2	48.4	0.14
	6	22.9	4.6	20.7	3.2	48.6	0.16
	7	22.9	4.6	20.7	3.2	48.6	0.47
	8	23.0	4.6	20.8	3.2	48.4	0.49
	9	22.9	4.6	20.7	3.2	48.6	0.79
	10	23.0	4.6	20.8	3.2	48.4	0.81
15	Sample	Physical Properties of Hydrogel					
		% H ₂ O	Clarity	Wettability	Strength		
	1	45.4	Clear	A	4		
	2	43.4	Clear	A	4		
	3	46.4	Clear	A	3		
	4	45.5	Clear	A	3		
	5	46.3	Clear	A	3-4		
	6	42.7	Clear	A	3-4		
	7	45.7	Clear	A	2		
	8	45.9	Clear	A	2		
20	9	48.0	Clear	A	2		
	10	43.8	Clear	A	2		
25							

As shown above, increasing initiator level to at least 0.47 % improves the strength of the resultant hydrogels.

Example 7:

This example shows the effect of chain extension of the polydimethyl siloxane (Z₁), prior to synthesis of the diadduct, on the resultant hydrogels.

3.0068 g (0.0014 mole) Shin-Etsu X-61-504A (1000) (MW 2212) are combined with 0.1512 g (0.0007 mole) IPDI and 0.5 microliters of DBTL and stirred overnight at room temperature. IR indicates complete reaction of the isocyanate functionality. This chain extended Z₁ is subsequently capped with IPDI and PEG as described in example 1 using PEG 1000 except for (sample 3). Sample 3 is heated at 50 °C for 72 hours, (rather than overnight) during the reaction with PEG. The calculated amount of IEM is then added to form (Z₁-IPDI-Z₁)_n{IPDI-PEG-IEM}₂. The IEM is reacted at room temperature overnight with stirring except for sample 1 which is heated at 35 °C.

Sample	Wt.% In the Polymerization Mixture					
	Z-	IPOI	PEG 1000	IEM	Solvent	BME
1	25.6	3.8	11.6	1.8	57.1 (1)	0.12
2	30.1	4.6	13.6	2.1	49.6 (2)	0.14
3	24.4	3.7	11.1	1.8	59.0 (2)	0.16
4	30.4	4.6	13.5	2.1	49.4 (3)	0.10

solvents:(1) = isopropyl acetate, (2) = acetone, (3) = methyl ethyl ketone.

Sample	Physical Properties of Hydrogel				
	% H ₂ O Content	Clarity	Wettability	Strength	DK (barrier)
1	40.8	Opaque	A	1-2	71.0
2	36.4	Hazy	A	1-2	105.2
3	43.1	Very Sl. Hazy	A	1-2	-
4	37.8	Hazy	A	1-2	103.5

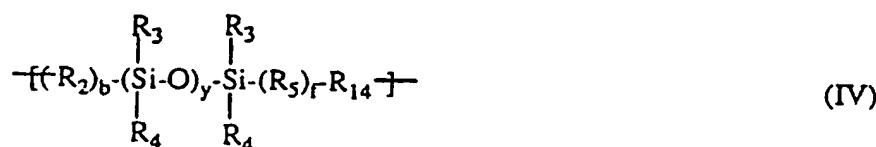
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Example 8:

- 25 This example demonstrates the fabrication of prototype polydimethylsiloxane/polyether lenses from polypropylene contact lens molds. The reaction solution is made as in example 3 (sample 5) using Shin-Etsu X-61-504A (1000) MW = 2400 and 0.78 % BME. The solution is pipetted into the lens molds and UV cured for 3 hours. After extraction in water and boiling, optically clear, strong lenses are obtained.
30 Young's modulus 15.9 kg/cm² and a 25% elongation.

Claims

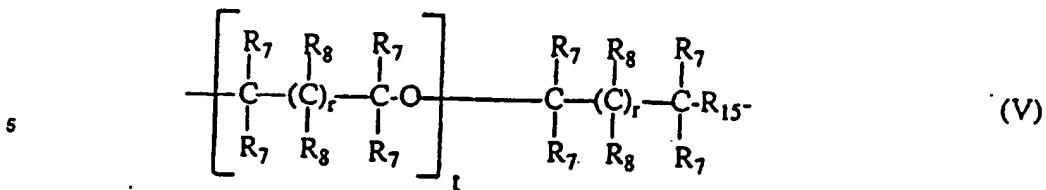
- 35 1. A macromer comprising a segment, Seg. of the formula
 $\{R_{14}-Sil-[L]_h-R_{14}-Sil\}_n(L)_h-R_{15}-A-[L-R_{15}-A]_m\}$ (I)
wherein R₁₄ is a bond or -N(R₁₅)-, or if R₁₄ is not attached to a silicon atom, then R₁₄ may also be -O-; R₁₅ is -O- or -N(R₁₆)-;
R₁₆ is hydrogen, C₁₋₆alkyl, or phenyl;
40 n is zero to 3;
m is zero to 3;
h is 1, or h may be zero when the atom of Sil to which it would otherwise be attached is carbon;
each Sil is independently of the formula



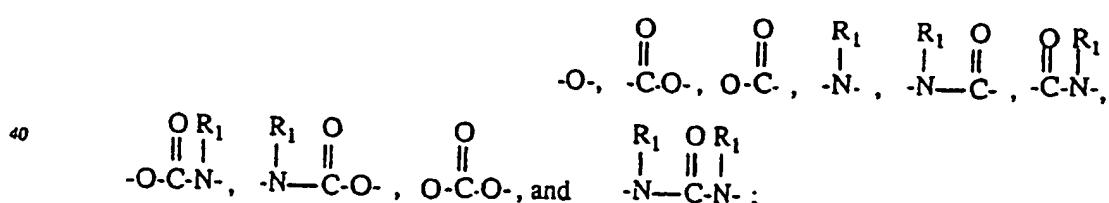
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each L is independently of the formula
-L₁R₆L₂-
and each A is independently of the formula

55



- 10 wherein within formula IV each R_2 and each R_5 is independently branched C_3 -alkylene, carbonyl, C_1 - ω alkylene carbonyl, C_1 - ω alkylene-(oxy- C_1 - ω alkylene) $_g$, or C_1 - ω alkylene-OCH₂-(hydroxy C_1 - ω alkylene)-CH₂;
- 15 with g being an integer of from 1 to 10;
each b and each f is independently 0 or 1;
each y is independently 1 to 200;
- 20 and each R_3 and each R_4 is independently selected from C_1 - ω alkyl and aryl of up to 12 carbon atoms;
and within L:
each L_1 and L_2 is independently
- 25 $\begin{array}{c} O \\ || \\ - CO- \text{ or } \end{array}$
 $\begin{array}{c} O \\ || \\ - CNH- \text{ in which the oxygen or nitrogen is bound to } R_6, \text{ or } \end{array}$
 $\begin{array}{c} O \\ || \\ - C- \text{ or a bond; and } \end{array}$
 each R_6 is independently
 (i) $-(C_1$ - ω aliphatic)- or
 (ii) a group of the formula
 $-(C_1$ - ω aliphatic)_j-Q_k-(5-7 membered cycloaliphatic or aryl of up to 25 carbon atoms)-Q_(k1)-(C_1 - ω aliphatic)_{j1}O- (IX),
 each of j, k, k1 and j1 being independently zero or one, but if j is 0, then k is 0 and if j1 is 0, then k1 is 0;
- 30 each D is 1 to 3;
each aliphatic group in the R_6 (i) or (ii) above is uninterrupted or interrupted at any point by Q;
each aliphatic, cycloaliphatic, and aryl group within the R_6 (i) or (ii) above is unsubstituted or substituted by one or more substituents which substituents are halogen, hydroxy, C_1 - ω alkyl, carboxy or C_1 - ω perhaloalkyl;
each Q is independently selected from
- 35



- 40 and within formula V:
 45 each r is independently 0-4;
 each t is independently 3-200; and
 each R_7 is independently selected from groups i) and iii) below and each R_8 is independently selected from groups i)-iv) below:
 i) hydrogen, halogen, unsubstituted C_1 - ω alkyl, substituted C_1 - ω alkyl, unsubstituted C_2 - ω alkenyl, and substituted C_2 - ω alkenyl, wherein a) the substituents on the alkyl and alkenyl groups in i) are independently selected from fluoro, C_1 - ω alkoxy, C_2 - ω alkanoyloxy, C_1 - ω alkoxy-C(O)-, C_2 - ω alkenyoxy-C(O)-, C_3 - ω alkenyoxy, aryl of up to 10 carbon atoms, aryloxy of up to 10 carbon atoms, aroyl of up to 11 carbon atoms, aroyloxy of up to 11 carbon atoms, aryl (of up to 10 carbon atoms)-oxycarbonyl, C_3 - ω cycloalkyl, C_3 - ω cycloalkoxy, (C_3 - ω cycloalkyl)-carbonyloxy, (C_3 - ω cycloalkoxy)carbonyl, oxacycloalkyl of up to 7 carbon atoms, oxacycloalkoxy of up to 7 carbon atoms, oxacycloalkoxy (of up to 7 carbon atoms)-carbonyl, and oxacycloalkyl (of up to 7 carbon atoms)-carbonyloxy; and b) each alkyl and alkenyl group in a) being unsubstituted or further substituted by fluoro, C_1 - ω alkyl, or C_1 - ω alkoxy provided that said last mentioned alkoxy is not bound to a carbon already singly bound to another oxygen atom; and

- ii) C_{1-16} alkoxy, C_{2-16} alkanoyloxy, C_{1-16} alkoxy-C(O)-, C_{2-16} alkenyloxy-C(O)- and C_{3-16} alkenoyloxy, each of which may be further substituted by fluoro, aryl of up to 10 carbon atoms, or C_{1-6} alkoxy provided that the last mentioned alkoxy is not bound to a carbon atom which is singly bound to another oxygen;

iii) aryl of up to 10 carbon atoms, C_{3-8} cycloalkyl, and oxacycloalkyl of up to 7 carbon atoms, each of which is unsubstituted or substituted by a substituent selected from those indicated in i)a) and b) above;

iv) aryloxy of up to 10 carbon atoms, cycloalkoxy of up to 8 carbons, cycloalkyl (of up to 8 carbons)-C(O)O-, cycloalkoxy (of up to 8 carbons)-carbonyl, aroyloxy of up to 11 carbons, oxacycloalkoxy of up to 7 carbons, oxacycloalkenyloxy of up to 7 carbons, oxacycloalkoxy (of up to 7 carbon atoms)-carbonyl, oxacycloalkyl (of up to 7 carbon atoms)-carbonyloxy, aryloxy of up to 11 carbon atoms, and aroyloxy of up to 11 carbon atoms, each of which is unsubstituted or substituted by fluoro, C_{1-6} alkyl, or C_{1-6} alkoxy, provided said last mentioned alkoxy is not bound to a carbon atom which is singly bound to another oxygen; and 2 adjacent groups R_7 and R_8 , together with the atoms to which they are attached may define a 5-8 membered cycloalkyl, cycloalkenyl, or oxacycloalkyl ring or a 6-14 membered bicyclo-ring.

2. The macromer of claim 1 comprising a segment, Grp, of the formula

$$\{R_{15}-A-[L-R_{15}-A]\}_m \quad (L)_h\overline{\gamma} \quad (\text{Seg}\cdot(L)_h)_p\cdot\text{Seg}\cdot((L)_h\cdot R_{14}\cdot\text{Sil}\cdot[(L)_h\cdot R_{14}\cdot\text{Sil}]_n)_e \quad (\text{II})$$

wherein R_{14} , R_{15} , L, Seg, Sil, h and A are as defined in claim 1;

m is an integer of zero to 10;

n is an integer of zero to 3;

p is an integer of zero to 7; and

a and e are each zero or 1, but a plus e is 1.

3. The macromer of claim 2 of the formula

$$\text{Cap-Grp-Cap} \quad (\text{III})$$

wherein Grp is as defined in claim 2;

each Cap is independently selected from formula VI or VII below provided at least one Cap per macromer is of formula VI; wherein formula VI is

$$R_{16}(L_4)_z(R_6)_w(A_1)_y(L_1)_x(J(R_9)_M(L_5)_G(R_6)_Y(L_6)_T\}_{\bar{Z}} \quad (\text{VI})$$

and formula VII is

$$R_{17}(L_4)_z(R_6)_w(A_1)_y(L_1)_x(J(R_9)_M(L_5)_G(R_6)_Y(L_6)_T\}_{\bar{Z}} \quad (\text{VII})$$

in which each R_6 is as defined in claim 1;

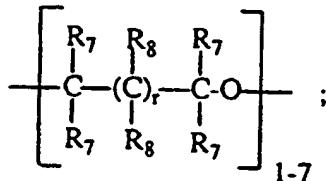
each w, x and z is independently zero or 1, but if w is zero, then one of x and z must be zero;

each G, M, T, V, Y and Z is independently zero or 1, but if Y is 0, then G must be zero and M must be one;

each J is -O- or -NH-;

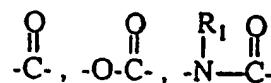
each A_1 and R_9 is independently of the formula

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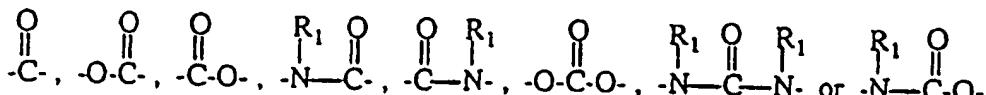


each L_3 is independently

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- 50 with the right hand portion attached to 'Grp' provided that the Grp atom to which L₃ is attached is not a carbonyl carbon, an amido nitrogen or a carboxy oxygen and L₃ is -O- or -NR₁- when such Grp atom is a carbonyl carbon;
each L is independently



when w is one, and selected from the same group as L₃ when w is zero;
 each L₅ is -C(O)NH- with the carbonyl attached R₉ to J;
 each L₆ is -C(O)NH- with the nitrogen attached to R₆ or R₉;
 each R₁₆ is independently of the formula

5



10

in which R₂ is hydrogen or C₁₋₇-alkyl and each of R₃ and R₄ is independently hydrogen, C₁₋₇-alkyl, or -COOR₁₃ with R₁₃ being hydrogen or C₁₋₄-alkyl; and R₁₇ is selected from

15 a) H, NH₂, OH, -NCO, -NCS, -C(O)-halogen and COOR₁₂ when the non-R₁₇ atom to which it is attached is a non-carbonyl saturated carbon or the non-R₁₇ atom to which it is attached is a carbon which is part of a ring;

b) H, -C(O)-halogen, -C(O)-R₂, -C(O)-OR₁₂ and R₁₂ when the non-R₁₇ atom to which it is attached is an oxygen other than a carboxy oxygen;

20 c) H and R₂, when the non-R₁₇ atom to which it is attached is a carboxy oxygen;

d) -C(O)-R₂, -C(O)-OR₁₂, -C(O)N(R₁)R₁₂ and R₂ when the non-R₁₇ atom to which it is attached is an amino nitrogen, or R₁₂ when the non-R₁₇ atom to which it is attached is an amido nitrogen;

e) OH, R₂, CH₂C(O)R₁₂, CH₂C(O)OR₁₂, NH₂, and -NHR₁₂ when the non-R₁₇ atom to which it is attached is a carboxy carbon; and

25 f) H, OH, hal, -OR₁₂ when the non-R₁₇ atom to which it is attached is silicon.

4. A macromer according to any of claims 1 to 3 wherein at least 30 % of the A blocks within any one macromer of formulae I-III are homopolymeric for not more than 15 repeating units.

5. A macromer according to claim 1 wherein Seg is represented by Seg₁ of formula {R₁₄-Sil-(L)_h-R₁₅-A} (Ia)

30 wherein R₁₄, R₁₅, Sil, L, A and h are as defined in claim 1.

6. A macromer according to claim 2 wherein Grp is represented by Grp₁ of formula {R₁₅-A-(L)_h}-Seg₁-{((L)_h-R₁₄-Sil)}_a (IIa)

wherein R₁₄, R₁₅, A, L, Sil, a and h are as defined in claim 2 and Seg₁ is as defined in claim 5.

7. A macromer according to claim 3 wherein Grp is represented by Grp₁ as defined in claim 6 and Cap is represented by Cap₁ of formulae R₁₆(L₄)_z(R₆)_w(A₁)_y(L₃)_x (VIa)

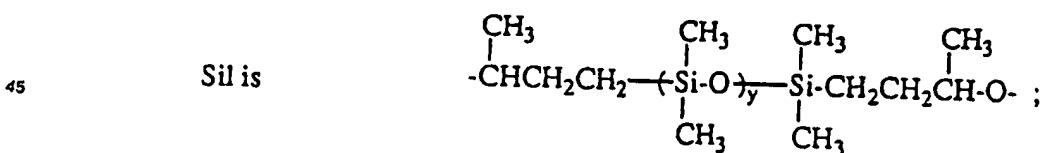
and

R₁₇(L₄)_z(R₆)_w(A₁)_y(L₃)_x (VIIa)

wherein all the variables are as defined in claim 3.

8. A macromer according to any of claims 5-7 wherein at least 30 % of the A blocks within any one macromer of formulae Ia, IIa or IIIa are homopolymeric for not more than 15 repeating units.

9. A macromer according to claim 3 wherein

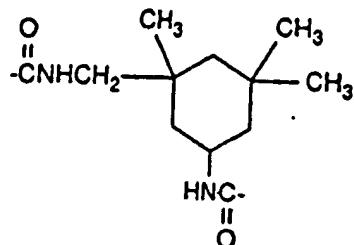


50 a is one;

e is zero;

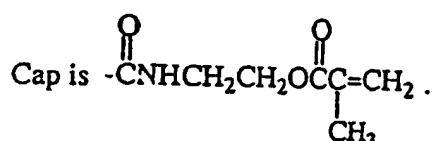
R₁₄ and R₁₅ are each -O-;

Lis



¹⁰ h is one;
A is $(\text{CH}_2\text{CH}_2\text{O})_n$; and
p is zero;
m is zero;

15



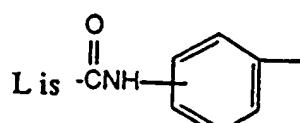
10. A macromer according to claim 4 wherein all the variables have the meaning as in claim 9.
11. A macromer of the formula
Cap-Sil-L-O-A-L-Sil-Cap

Cap-Sil-L-O-A-L-Sil-Cap

wherein Sil is $-\text{CH}_2\text{CH}_2-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{Si}-\text{O}}}-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{Si}-\text{CH}_2\text{CH}_2-}}$

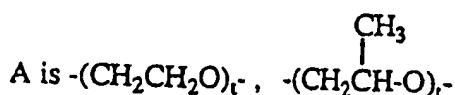
wherein y is 1 to 200, (especially y of about 4, 7 and about 16).

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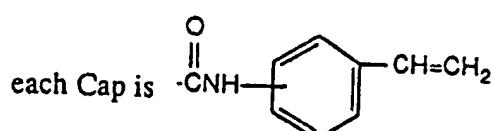


with the phenyl ring thereof bound to Si; m is zero to 3;

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50 wherein t is 3 to 200, or a poloxamer or reverse poloxamer having t polyoxyalkylene units per A group (especially t of about 6-8, about 45-55, and about 90-95); and



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12. A macromer according to claim 11 wherein all the variables have the meaning as defined in claim 11 and wherein at least 30 % of the A blocks are homopolymeric for not more than 15 repeating units.
13. A polymer fabricated from one or more macromers of any of claims 1 to 3 having in its fully swollen state a water content of at least 10 %.
14. A polymer fabricated from one or more macromers of claim 4 having in its fully swollen state a water content of at least 10 %.
15. A polymer fabricated from one or more macromers of any of claims 5 to 7 having in its fully swollen state a water content of at least 10 %.
16. A polymer fabricated from one or more macromers of claim 8 having in its fully swollen state a water content of at least 10 %.
17. A polymer fabricated from one or more macromers of claim 9 or 10 having in its fully swollen state a water content of at least 10 %.
18. A polymer fabricated from one or more macromers of claim 11 or 12 having in its fully swollen state a water content of at least 10 %.
19. A polymer being a copolymer of at least 10 % of one or more macromers of any of claims 1 to 3 and at least one copolymerizable monomer which is not a macromer of any of claim 1 to 3, having in its fully swollen state a water content of at least 10 %.
20. A polymer being a copolymer of one or more macromers of claim 4 and at least one copolymerizable monomer which is not a macromer of claim 4, having in its fully swollen state a water content of at least 10 %.
21. A polymer being a copolymer of at least 10 % of one or more macromers of any of claims 5 to 7 and at least one copolymerizable monomer which is not a macromer of any of claim 5 to 7, having in its fully swollen state a water content of at least 10 %.
22. A polymer being a copolymer of one or more macromers of claim 8 and at least one copolymerizable monomer which is not a macromer of claim 8, having in its fully swollen state a water content of at least 10 %.
23. A polymer being a copolymer of one or more macromers of claim 9 or 10 and at least one copolymerizable monomer which is not a macromer of claim 9 or 10, having in its fully swollen state a water content of at least 10 %.
24. A polymer being a copolymer of one or more macromers of claim 11 or 12 and at least one copolymerizable monomer which is not a macromer of claim 11 or 12, having in its fully swollen state a water content of at least 10 %.
25. An ophthalmic device comprising an optically clear polymer of claim 13 or 14.
26. An ophthalmic device comprising an optically clear polymer of claim 15 or 16.
27. An ophthalmic device comprising an optically clear polymer of claim 17.
28. An ophthalmic device comprising an optically clear polymer of claim 18.
29. An ophthalmic device comprising an optically clear polymer of claim 19 or 20.
30. An ophthalmic device comprising an optically clear polymer of claim 21 or 22.
31. An ophthalmic device comprising an optically clear polymer of claim 23.
32. An ophthalmic device comprising an optically clear polymer of claim 24.
33. The ophthalmic device of any of claims 25, 26, 29 or 30 which is a contact lens.
34. The ophthalmic device of any of claims 27 or 31 which is a contact lens.
35. The ophthalmic device of any of claims 28 or 32 which is a contact lens.
36. A method of correcting visual defects comprising applying to a patient in need thereof a visual defect correcting ophthalmic device of claim 25.
37. A method of changing eye color comprising applying to a patient a colored contact lens of claim 33.